CUMULANT EXPANSION METHOD IN THE DENSITY MATRIX APPROACH TO WAVE PACKET DYNAMICS IN MOLECULAR SYSTEMS

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A non-Markovian master equation for a molecule interacting with a heat bath is obtained using the cumulant expansion method. The equation is applied to the problem of molecular wave packet relaxtional dynamics. An exact solution is derived that demonstrates classical type of squeezing for the wave packet evolution and a heat-bath dependent frequency shift.

1 Introduction and model Hamiltonian

The problem of relaxational dynamics of wave packets in molecular systems is one of the up-to-date physical problems supported by femtosecond-time-scale spectroscopic facilities[1] as well as by single molecule spectroscopy.[2] Numerous theoretical investigations of the problem appeal to different approaches.[3] Due to the complexity of molecular relaxational dynamics a derivation of an exactly solving model for the problem has not been obtained yet. In this paper we investigate one of the models based on a master equation approach.

We will start from the general potential for a single molecule interacting with a bath of harmonic oscillators. After the derivation of the general master equation we will proceed to the specific example of harmonic potential for the model, which admits an exact solution.

The molecule interacting with a heat bath is separated into relevant system of diabatic vibronic levels E_μ and the environment of the heat bath modes ξ with frequency ω_ξ, and creation operator b_ξ^+. It is modelled by the Hamiltonian $H = H^S + H^E + H^{SE}$, with

$$\begin{aligned} H^S &= \textstyle\sum_\mu E_\mu d_{\mu\mu} + \hbar \sum_{\mu\nu} v_{\mu\nu} d_{\mu\nu} \\ H^E &= \textstyle\sum_\xi \hbar\omega_\xi \left(b_\xi^+ b_\xi + 1/2 \right), \\ H^{SE} &= \textstyle\sum_{\mu\nu} \hbar \left(r_{\mu\nu} + r_{\mu\nu}^+ \right) d_{\mu\nu}, \end{aligned} \tag{1}$$

where $d_{\mu\nu} = |\mu\rangle \langle\nu|$ is the transition operator of the system; $r_{\mu\nu} = \sum_\xi \mathcal{K}_{\mu\nu}^\xi b_\xi$ is annihilation operator of the bath including the matrix elements $K_{\mu\nu}^\xi$ of interaction function K^ξ. This model was discussed previously[3] and an equation of motion for the reduced density matrix σ was derived taking the system-environment coupling into account by perturbation theory. In our approach to the reduced density matrix equation we use the cumulant expansion method.[4] The applicability of this method

is rather wide because it does not appeals to perturbation theories motivation but relates to the statistical aspects of the influences of the heat bath.

2 Master equation and its reduced form for the harmonic potential

The second order cumulant expansion[4] gives[5]

$$\begin{array}{rcl} \dot{\sigma} & = & -\frac{i}{\hbar}[H^S,\sigma] + \exp\left(-\frac{i}{\hbar}H^S t\right)\dot{\mathbf{K}} exp\left(\frac{i}{\hbar}H^S t\right)\sigma, \\ \dot{\mathbf{K}}\sigma & = & \left(-\frac{i}{\hbar}\right)^2 \int_0^t d\tau \left\langle [\tilde{H}^{ES}(t),[\tilde{H}^{ES}(\tau),\sigma]] \right\rangle, \end{array} \tag{2}$$

where angle brackets mean averaging over environment and $\tilde{H}^{ES}$ is the Hamiltonian in interaction picture. This approach allows us to describe non-Markovian processes, when such factors as $\exp i\omega_{k\lambda}(\tau - t)$ (where $\omega_{k\lambda} = H^S_{k\lambda}/\hbar$) contain memory effects. We obtain for the matrix elements[5]

$$\begin{array}{rl} \dot{\sigma}_{\mu\nu} = -\frac{i}{\hbar}[H_0^S,\sigma]_{\mu\nu} - \int\limits_0^t d\tau \sum\limits_{k\lambda} & [(\left\langle r_{\mu\kappa}(t)r^+_{\kappa\lambda}(\tau)\right\rangle + \left\langle r^+_{\mu\kappa}(t)r_{\kappa\lambda}(\tau)\right\rangle)e^{i\omega_{k\lambda}(\tau-t)}\sigma_{\lambda\nu} \\ & -(\left\langle r_{\lambda\nu}(\tau)r^+_{\mu\kappa}(t)\right\rangle + \left\langle r^+_{\lambda\nu}(\tau)r_{\mu\kappa}(t)\right\rangle)\sigma_{\kappa\lambda}e^{i\omega_{\lambda\nu}(\tau-t)} \\ & -(\left\langle r_{\lambda\nu}(t)r^+_{\mu\kappa}(\tau)\right\rangle + \left\langle r^+_{\lambda\nu}(t)r_{\mu\kappa}(\tau)\right\rangle)e^{i\omega_{\mu\lambda}(\tau-t)}\sigma_{\kappa\lambda} \\ & +(\left\langle r_{\kappa\lambda}(\tau)r^+_{\lambda\nu}(t)\right\rangle + \left\langle r^+_{\kappa\lambda}(\tau)r_{\lambda\nu}(t)\right\rangle)\sigma_{\mu\kappa}e^{i\omega_{k\lambda}(\tau-t)}]. \end{array}$$

Using the Markov approximation the master equation reads[5]

$$\begin{array}{rl} \dot{\sigma}_{\mu\nu} = -\frac{i}{\hbar}\left[H_0^S,\sigma\right]_{\mu\nu} - \pi\sum\limits_{\kappa\lambda}\sum\limits_{\xi} & [\mathcal{K}^\xi_{\mu k}\mathcal{K}^\xi_{k\lambda}\left\{(1+n_\xi)\,\delta(\omega_{k\lambda}+\omega_\xi) + n_\xi\delta(\omega_{k\lambda}-\omega_\xi)\right\}\sigma_{\lambda\nu} \\ & -\mathcal{K}^\xi_{\lambda\nu}\mathcal{K}^\xi_{\mu\kappa}\left\{(1+n_\xi)\,\delta(\omega_{\lambda\nu}-\omega_\xi) + n_\xi\delta(\omega_{\lambda v}+\omega_\xi)\right\}\sigma_{\kappa\lambda} \\ & -\mathcal{K}^\xi_{\lambda\nu}\mathcal{K}^\xi_{\mu\kappa}\left\{(1+n_\xi)\,\delta(\omega_{\mu\lambda}+\omega_\xi) + n_\xi\delta(\omega_{\mu\lambda}-\omega_\xi)\right\}\sigma_{k\lambda} \\ & +\mathcal{K}^\xi_{\kappa\lambda}\mathcal{K}^\xi_{\lambda\nu}\left\{(1+n_\xi)\,\delta(\omega_{k\lambda}-\omega_\xi) + n_\xi\delta(\omega_{k\lambda}+\omega_\xi)\right\}\sigma_{\mu\kappa}]. \end{array}$$

In the following we apply this approach to a system with a harmonic oscillator potential. In the interacrion picture the respective Hamiltonian of interaction reads

$$\tilde{H}^{ES}(t) \;=\; \sum\nolimits_\xi K^\xi\left(b^+_\xi(t) + b_\xi(t)\right)\left(a^+(t) + a(t)\right). \tag{3}$$

We also suggested , that there are no negative frequencies in bath. Returning to the Schrödinger picture we can finally write the master equation for a damped harmonic oscillator [5]

$$\begin{array}{rl} \dot{\sigma} = -i\omega\left[a^+a,\sigma\right] & +\gamma n\left(\left[\left(a^+ + a\right),\sigma a\right] + \left[a^+\sigma,\left(a^+ + a\right)\right]\right) \\ & +\gamma(n+1)\left(\left[\left(a^+ + a\right),\sigma a^+\right] + \left[a\sigma,\left(a^+ + a\right)\right]\right), \end{array} \tag{4}$$

with damping rate $\gamma n = \pi\left(K^\xi\right)^2\rho(\omega)\,n(\omega)$, ρ means density of bath states. It should be noted that this master equation differs from the usual form of the master equation for the damped harmonic oscillator[6]. The differences are the result of the

full form of the molecule-bath interaction. Usually rotating wave approximation form of this Hamiltonian is used. The presence of the counter-rotating terms[5] in the Hamiltonian leads to the phase-dependent terms in the master equation which connect diagonal matrix elements σ_{nn} and non-diagonal ones σ_{mn}. The later describes the phase-dependent effects.

3 Method of solution and analytical results

The solution is based on an application of the characteristic function $F(\lambda, \lambda^*, t) = Sp(f\sigma)$, where $f = e^{\lambda a^+} e^{-\lambda^* a}$. Evaluating as usually commutators like $[a, \exp(\lambda a^+)]$ one finds[5]: $Sp([a^+ a, \sigma] f) = (\lambda^* \partial_{\lambda^*} - \lambda \partial_\lambda) F$, $Sp([a^+, \sigma a] f) = \lambda (\partial_{\lambda^*} - \lambda) F$, $Sp([a^+, \sigma a^+] f) = -\lambda^* \partial_\lambda F$, and etc. This allows us to transfer the operator equation (4) into the c-number differential equation with partial derivatives

$$\dot{F} = \left(-\left(i\omega\lambda^* + \gamma(\lambda^* + \lambda)\right) \partial_{\lambda^*} + \left(i\omega\lambda - \gamma(\lambda^* + \lambda)\right) \partial_\lambda - \gamma n \left\{\lambda + \lambda^*\right\}^2 \right) F. \tag{5}$$

The solution of the equation is obvious. We solve it by expanding $F(\lambda, \lambda^*, t) = \exp\left(\sum_{m,n} K_{mn}(t) \lambda^m (-\lambda^*)^n\right)$. Substitution F in this form into (5) gives a set of independent systems of differential equations (SODE)[5] for functions K_{mn} with $m + n = N$ being a fixed number. The first two systems are:

$$\begin{aligned} \dot{K}_{10} &= (i\omega - \gamma) K_{10} + \gamma K_{01}, \\ \dot{K}_{01} &= \gamma K_{10} + (-i\omega - \gamma) K_{01}, \end{aligned} \qquad \begin{aligned} \dot{K}_{11} &= 2\gamma(n - K_{11}) + 2\gamma(K_{02} + K_{20}), \\ \dot{K}_{20} &= -\gamma(n - K_{11}) + 2(i\omega - \gamma) K_{20}, \\ \dot{K}_{02} &= -\gamma(n - K_{11}) - 2(i\omega + \gamma) K_{02}. \end{aligned}$$

For a wide class of initial states (coherent, thermal, squeezed, etc.) the consideration can be restricted by these two systems, because all higher-order elements of K_{mn} are zero. Below we choose the coherent state as initial one. For this initial state the solutions of these SODEs read

$$\begin{aligned} K_{10} + K_{01} &= Q_0 e^{-\gamma t} \left[(\gamma/\tilde{\omega}) \sin\tilde{\omega}t + \cos\tilde{\omega}t \right], \\ K_{11} + K_{20} + K_{02} &= n - n e^{-2\gamma t} \left[1 + (\gamma/\tilde{\omega})^2 (1 - \cos 2\tilde{\omega}t) + (\gamma/\tilde{\omega}) \sin 2\tilde{\omega}t \right], \end{aligned} \tag{6}$$

where $\tilde{\omega} = \sqrt{\omega^2 - \gamma^2}$, $n = (\exp(\hbar\omega/k_B T) - 1)^{-1}$ and Q_0 is initial coherent state coordinate. The distribution of interest in coordinate space is $P(Q, t)=$ $\frac{1}{2\pi} \int_{-\infty}^{\infty} d\lambda e^{-i\lambda Q} \chi(\lambda, t)$, where $\chi(\lambda, t) = Sp\left(e^{i\lambda\left(a^+ + a\right)} \sigma(t)\right) = e^{-\frac{1}{2}\lambda^2} F(i\lambda, -i\lambda, t)$. Integration yields

$$P(Q,t) = \frac{2}{\sqrt{\pi\left(\frac{1}{2} + K_{20} + K_{02} + K_{11}\right)}} \exp\left\{ -\frac{(Q - K_{10} - K_{01})^2}{\frac{1}{2} + K_{20} + K_{02} + K_{11}} \right\}. \tag{7}$$

Fig. 1. The plots show wave packet dynamics $\gamma = 0.1\omega$, $k_B T = 3\hbar\omega$, $\omega t = (0:20)$, $Q_0 = 4$ (a); and the variance of the wave packet (b).

The obtained exact solution $P(Q,t)$ shows some kind of classical squeezing because the width of the wave packet slightly oscillates in time instead of it's monotone increasing for usual damping processes. This squeezing which is displayed in Fig.1 has not been derived previously. It should be stressed that this is not quantum squeezing because this width is never smaller than the ground state width. Eq.6 demonstrates a decrease of the effective harmonic oscillator frequency due to the phase-dependent interaction with the bath. This prediction is also new.

The consideration of more complex potentials on the basis of proposed generalized master equations is now in progress.

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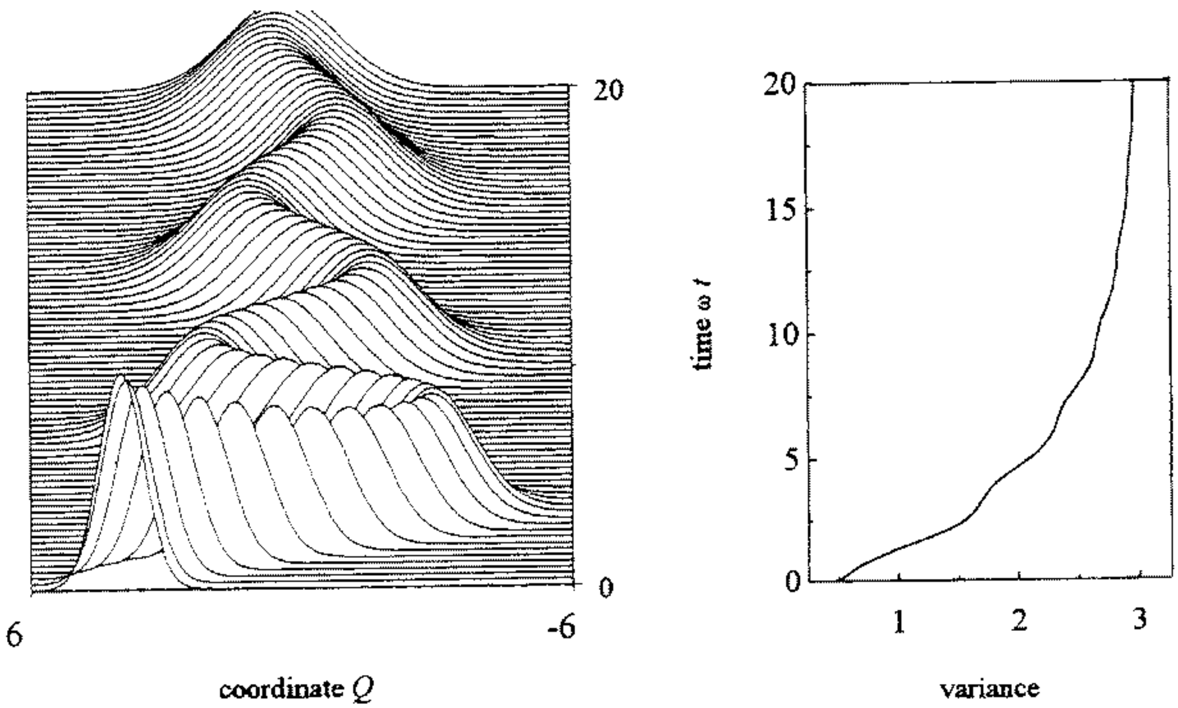

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